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Standard enthalpies of formation of some lutetium alloys by high-temperature direct synthesis calorimetry

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Abstract

The standard enthalpies of formation for some lutetium alloys in the binary systems Lu–X (where X = C, Si, Ge, Sn, B, Al) have been determined by direct synthesis calorimetry at 1473±2 K. The following values of ΔH_f° in kJ g.atom^{-1} are reported: LuC_2 −26.7±1.8; LuSi −78.3±2.1; Lu_5Ge_3 −73.8±1.5; Lu_5Sn_3 −73.6±1.4; LuB_2 −29.8±0.9; $LuAl_2$ −52.6±3.0; GdSi = −75.6±2.3. The results are compared with some earlier experimental data derived from e.m.f. or mass spectrometric measurements, with predicted values from Miedema's semi-empirical model and with reported calorimetric data for the corresponding compounds of some early lanthanide elements.

Keywords: Formation enthalpies; Lu alloys; Direct synthesis calorimetry

1. Introduction

During recent years we have in this laboratory conducted systematic studies of the thermochemistry of rare earth carbides, silicides, germanides and borides using high temperature calorimetric methods [1]. These investigations began with the work of Topor and Kleppa on LaB_6, Sc_5Si_3, Y_5Si_3 and Lu_5Si_3 based on solute solvent drop calorimetry [2–4], and on Sc_5Ge_3, Y_5Ge_3 and La_5Ge_3 by Jung and Kleppa using the same technique [5]. During the past year this study has been extended by the present authors to the enthalpies of formation of the group IIIA carbides [6] and most recently to the carbides, silicides, germanides and borides of the lanthanide elements La, Ce, Pr, Nd and Gd [7–9]. In the present study we report new thermochemical data for some compounds in the binary systems Lu–C, Lu–Si, Lu–Ge, Lu–Sn, Lu–B and Lu–Al. In addition to these, we also report the enthalpy of formation for GdSi which was not included in our previous communication [8].

The information in the literature regarding the considered phases is less extensive than for the compounds of the corresponding early lanthanide elements. For example, there is no established phase diagram for the Lu–C system, and the phase diagrams for Lu–Si and Lu–Sn are incomplete [10]. For this reason the melting points were not available for three of the six compounds which we studied [10]. Information regarding the structural properties are generally available [11–17]. However, the X-ray diffraction data for three of the six compounds were not included in the ASTM powder diffraction file.

The published literature offers a value for the heat of formation of LuC_2 calculated from mass spectrometric data [18], and for $LuSn_3$ based on e.m.f. measurements [19]. However, we found no experimental values for the enthalpies of formation in the Lu–Si, Lu–B and Lu–Al systems. We mentioned already that a calorimetric value for Lu_5Si_3 is available [4]. We will compare our new enthalpy data with the derived e.m.f. and mass spectrometric values and with the predictions based on Miedema's semi-empirical model [20]. We will also compare our results for $LuAl_2$ and Lu_5Sn_3 with published values for the corresponding alloys of the earlier lanthanides [21–25]. Since Lu is the end member of the lanthanide elements, our new thermochemical data allow us to assess possible systematic changes in the enthalpies of formation of these alloys. Our new data also allow us to further test the systematic correlation of the heats of formation of compounds of the lanthanide elements with compounds of the elements in the IIIB and IVB columns of the periodic table [26–28].

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2. Experimental and materials

The experiments were carried out at 1473±2 K in a single unit differential microcalorimeter which has been described in an earlier communication from this laboratory [29]. All the experiments were performed under the protective atmosphere of argon gas, purified by passing it over titanium chips at about 900 °C. A boron nitride crucible was used to contain the samples.

All the materials except B were purchased from Johnson Matthey/Aesar, Ward Hill, MA; Lu was in ingot form; B was obtained from Alfa Products/Ventron. The purities of the samples ranged from 99.0% for C to 99.999% for Ge. The particle size of the powders used was about −80 mesh for Lu, −100 mesh for Sn, −150 mesh for Ge, −300 mesh for C and −325 mesh for Si and Al. In order to avoid as much as possible any oxidation by air the Lu samples were hand-filed from the ingot immediately prior to the preparation of the sample pellets. The C was in the crystalline graphite modification. As purchased, the Ge sample had an average particle size of −10 mesh. We ground this sample in an agate mortar and sifted it through a 150 mesh sieve. The B sample consisted of the crystalline material in the rhombohedral form. To obtain a particle size suitable for the calorimetric experiments, this was ground in an agate mortar and sifted through a 150 mesh sieve.

The two components were carefully mixed in the appropriate molar ratio, pressed into 4 mm pellets and dropped into the calorimeter from room temperature. In a subsequent set of experiments the reaction products were dropped into the calorimeter from room temperature to measure their heat contents. Between the two sets of experiments the samples were kept in a vacuum dessicator to prevent reaction with oxygen or moisture.

Calibration of the calorimeter was achieved by dropping weighed segments of 2 mm outer diameter high purity Cu wire from room temperature into the calorimeter at 1473±2 K. The enthalpy of pure Cu at this temperature, 46 465 J $g.atom^{-1}$, was obtained from Hultgren et al. [30]. The calibrations were reproducible to within ±1.2%.

The reacted samples were examined by X-ray diffraction to assess their structures and to ascertain the absence of unreacted metals. Some of the samples were also subjected to SEM and X-ray microprobe analysis. As we noted in an earlier communication [6], the rare earth carbides, since they decompose on mounting, cannot be tested by this method.

While the melting point of LuC_2 is not known, the reported eutectic temperature of LuC_2–C is about 2230 °C [31]. LuC_2 undergoes a structural transformation from tetragonal to cubic at about 1450±55 °C. We prepared LuC_2 according to the procedure which we described in detail for other rare earth carbides in our earlier communication [6]. We found that this compound is extremely sensitive to moisture and oxygen in the air. Even though the sample for powder diffraction was prepared immediately after removal from a vacuum dessicator and was coated heavily with vaseline, we observed some decomposition during the time of the diffraction analysis. The diffraction pattern matched well that of the low temperature tetragonal modification listed in the ASTM powder diffraction file. However, after the first 30 min, Lu_2O_3 as well as free C, could be identified. There was no evidence for the presence of unreacted metal or other carbide phases.

The phase diagram of the Lu–Si system is not complete. However, it indicates the existence of Lu_5Si_3 and LuSi and Lu_3Si_5 or $LuSi_2$ [10]. The enthalpy of formation of Lu_5Si_3 has already been determined by Topor and Kleppa by solute–solvent drop calorimetry [4]. There is no information about the melting points of these compounds. We prepared both LuSi and $LuSi_2$ in the calorimeter. However, the X-ray diffraction pattern of $LuSi_2$ showed a mixed phase with the predominant compound being LuSi. The pattern for LuSi is not listed in the ASTM powder diffraction file. The X-ray diffraction pattern of our LuSi sample agreed well with a pattern generated from its unit cell parameters and the atomic coordinates of the structural prototype CrB. However, in this sample we also observed two minor phases, namely less than 1% of Lu_5Si_3 and less than 5% of $LuSi_2$.

The phase diagram of the Lu–Ge system shows one congruently melting phase, Lu_5Ge_3 which melts at 2040 °C [10]. The X-ray diffraction pattern of this phase is not available in the ASTM powder diffraction file and its atomic coordinates are not available [32]. We therefore generated a pattern from its unit cell parameters and atomic coordinates consistent with its structure type Mn_5Si_3. Our X-ray diffraction pattern matched well the generated pattern. There was no evidence for the presence of unreacted metal or even of the oxide. However, we observed one minor unidentified peak. SEM and X-ray microprobe analysis indicated that this compound was single phase.

The phase diagram of the Lu–Sn system is incomplete. However, it shows the existence of three compounds, Lu_5Sn_3, $LuSn_2$ and $LuSn_3$ [10]. The composition of the latter compound is uncertain [10]. Structural information is available only for Lu_5Sn_3 and $LuSn_2$ [11,12]. Since the X-ray diffraction pattern of Lu_5Sn_3 is not listed in the ASTM powder diffraction file, we generated a pattern from its unit cell parameters and the atomic coordinates of the structural prototype Mn_5Si_3. The generated pattern agreed well with our experimental pattern. There was no evidence for the presence of unreacted metal or other phases, not even of the oxide.

The phase diagram of the Lu–B system shows the existence of the congruently melting compound LuB_4 and several peritectic phases. Among these we selected LuB_2 for study. This phase has the hexagonal AlB_2 structure, and its lattice parameters are in close agreement with the corresponding values for DyB_2; its *c*/*a* ratio is nearly identical with those of GdB_2 and YB_2 [17]. We also attempted to prepare LuB_4. However, this sample showed a mixed phase, with a major presence of LuB_2.

We observed no unreacted metal or oxide in our LuB_2 sample. Its X-ray diffraction pattern showed good agreement with the pattern in the ASTM powder diffraction file. However, we also found approximately 10–15% LuB_4. SEM and X-ray microprobe analysis also showed two phases, with the minor phase present in about 10%.

The phase diagram of the Lu–Al system shows two congruently melting phases, $LuAl_2$ and Lu_3Al_2 [10]. We prepared $LuAl_2$ in the calorimeter since this composition is the predominant one for all the lanthanide aluminides. $LuAl_2$ melts at 1500 °C [10,33]. Its X-ray diffraction pattern agreed well with the pattern listed in the ASTM powder diffraction file. While we observed about 1% Lu_2O_3 and 1–2% of a second phase in the X-ray pattern, the SEM and the X-ray microprobe analysis indicated that the compound was essentially single phase.

The phase diagram of the Gd–Si system shows four congruently melting compounds [10]. We already reported the enthalpies of formation of Gd_5Si_3 and $GdSi_2$ [8]. The melting point of GdSi is not reported in the phase diagram. The X-ray diffraction pattern of GdSi is not listed in the ASTM powder diffraction file, nor are its atomic coordinates available. For this reason we generated its diffraction pattern using the unit cell parameters of GdSi and the atomic coordinates of its structural prototype FeB. The generated and experimental patterns matched well; however, we noticed the presence of less than 5% of $GdSi_2$. In reported X-ray diffraction patterns of GdSi we noted that this phase undergoes a solid state transformation at room temperature. We observed the presence of increasing amounts of $GdSi_2$ over a period of five days.

3. Results and discussion

The standard enthalpies of formation of the rare earth alloys determined in this study were obtained as the difference between the results of two sets of measurements. In the first set the following reaction takes place in the calorimeter:

$$\mathrm{RE(s,298K)} + m\mathrm{X(s,298\ K)} = \mathrm{REX}_m\mathrm{(s,1473\ K)} \qquad (1)$$

Here *m* represents the molar ratio X/RE; RE is the considered rare earth metal, while X represents C, Si, Ge, Sn, B or Al and s denotes solid. The reacted pellets were reused in a subsequent set of measurements to determine their heat contents:

$$\mathrm{REX}_m\mathrm{(s,298\ K)} = \mathrm{REX}_m\mathrm{(s,1473\ K)} \qquad (2)$$

The standard enthalpy of formation is given by:

$$\Delta H^0_f = \Delta H(1) - \Delta H(2) \qquad (3)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the enthalpy changes per g.atom of compound associated with reactions (1) and (2).

The experimental results are summarized in Table 1. The heat effects associated with reactions (1) and (2) are given in kJ g.atom^{-1} as the average of five to seven consecutive measurements with the appropriate standard deviations. The last column shows the standard enthalpy of formation of the considered phases. The standard deviations given in the last column also reflect a contribution from the uncertainties in the calibrations. For LuC_2 we were not able to measure the heat content of the alloy, since we observed extensive decomposition during the few minutes used to transfer and weigh the carbide samples. For this reason we measured the heat content of the Lu metal and calculated the heat content of the compound using the Kopp–Neumann rule. The heat content of C was taken from Hultgren's compilation of thermodynamic data to be 22.595 kJ g.atom^{-1} at 1473 K [30]. Therefore the value of ΔH^0_f for LuC_2 in Table 1 is a partly experimental, partly calculated quantity.

Table 2 compares the standard enthalpies of formation reported in the present work with experimental values from the published literature and with predicted values from Miedema's semi-empirical model [20]. It should be noted that the earlier experimental data for the compounds we studied were derived from e.m.f. or mass spectrometric measurements. We found no calorimetric data. Our measurement for the enthalpy of formation of LuC_2 is considerably less exothermic than the value given by Guido et al. based on mass spectrometry [18]; however, it compares well with the

Table 1
Summary of the standard enthalpies of formation for some Lu alloys and for GdSi (kJ g.atom^{-1}); numbers in parentheses indicate numbers of experiments averaged

Compound	$\Delta H(1)$	$\Delta H(2)$	ΔH^0_f
LuC_2	$+1.3 \pm 0.9(6)$	$28.0 \pm 1.4(6)$	-26.7 ± 1.8
LuSi	$-49.6 \pm 1.2(5)$	$28.7 \pm 1.6(5)$	-78.3 ± 2.1
Lu_5Ge_3	$-43.6 \pm 0.8(5)$	$30.2 \pm 0.5(5)$	-73.8 ± 1.5
Lu_5Sn_3	$-41.8 \pm 0.9(6)$	$31.8 \pm 0.7(5)$	-73.6 ± 1.4
LuB_2	$-1.8 \pm 0.4(5)$	$28.0 \pm 0.6(6)$	-29.8 ± 0.9
$LuAl_2$	$-20.4 \pm 2.0(5)$	$32.2 \pm 2.1(6)$	-52.6 ± 3.0
GdSi	$-46.0 \pm 0.9(6)$	$29.6 \pm 2.1(6)$	-75.6 ± 2.3

Table 2
Comparison of the new enthalpies of formation with data in the literature and with predicted values from Miedema's semi-empirical model; data in kJ g.atom^{-1}

Compound	m_p (°C)	ΔH_f^0 (expt.)		Method	ΔH_f^0(pred.)
		this study	literature		
LuC_2		-26.7 ± 1.8	-39.1 ± 7.0	Mass spectrometry [18]	-69
LuSi		-78.3 ± 2.1			-80
Lu_5Si_3			-67.8 ± 3.3	calorimetry [2]	-68
Lu_5Ge_3	2040	-73.8 ± 1.5			-75
Lu_5Sn_3		-73.6 ± 1.4			-80
$LuSn_3$	1017		-39.1 ± 0.8	e.m.f. [19]	-55
LuB_2	2250	-29.8 ± 0.9			-69
$LuAl_2$	1800	-52.6 ± 3.0			-63
GdSi		-75.6 ± 2.3			-78

values for earlier lanthanide dicarbides measured by the present authors [6–8].

While there is no published value for the heat of formation of LuSi, our value for this compound is somewhat more exothermic than the value for Lu_5Si_3 reported by Topor and Kleppa based on solute–solvent drop calorimetry [4]. Since there is no detailed phase diagram available, we cannot make a comparison of the melting points. However, if we assume that the heat of formation varies in the simplest possible way with composition, we would expect the 1:1 molar ratio to yield a more exothermic value than the 5:3 ratio.

We found no information in the published literature regarding the enthalpies of formation of Lu_5Ge_3 and Lu_5Sn_3. However, our value for Lu_5Ge_3 is very similar to the values we found for the corresponding germanides formed by the earlier lanthanide elements [7,8]. In the Lu–Sn system, a heat of formation for $LuSn_3$ is reported by Bayanov et al. based on e.m.f. measurements [19]. However, the phase diagram for this system suggests that there are doubts regarding the stoichiometry of $LuSn_3$ [10]. Only the structures of Lu_5Sn_3 and $LuSn_2$ are known [11,12]. The phase diagrams for the alloys of Sn with earlier lanthanide elements, for which detailed phase diagrams are known, show that the 5:3 ratio phases usually melt congruently and at considerably higher temperatures than the 1:2 or 1:3 ratio alloys. Therefore one might also expect the enthalpies of formation to be more exothermic for the 5:3 stoichiometry than for these other compounds.

There are no literature data for the enthalpy of formation of LuB_2. However, our value for this boride is roughly comparable with what we found for YB_2, -35.7 ± 2.6 kJ g.atom^{-1} [34].

There is no literature value for the enthalpy of formation of $LuAl_2$. However, Colinet et al. measured the enthalpies of formation for all the other rare earth aluminides by high temperature solution calorimetry [21]. Note that Eu and Yb are divalent metals while the other lanthanides are trivalent. With the exception of the numerically lower values for $EuAl_2$ and $YbAl_2$, the average of all the other enthalpies of formation is -52.8 ± 1.2 kJ g.atom^{-1}. Our new value for $LuAl_2$ fits very well within this range.

There is no literature value for the enthalpy of formation of GdSi. However, our value compares well with values for earlier lanthanide monosilicides measured by the present authors [6–8] and with our result for LuSi.

Table 2 shows that Miedema's predicted enthalpy of formation values are in reasonable agreement with our new measurements for LuSi, Lu_5Ge_3, Lu_5Sn_3 and GdSi. However, for $LuAl_2$ the predicted value is somewhat more exothermic than our experimental result. We noted already in our earlier work that the predicted values for carbides and borides differ very considerably from our experimental results [6–9].

In Fig. 1 we present a systematic graph which shows the standard enthalpies of formation of carbides, silicides and germanides of Lu compared with data for the corresponding alloys of the earlier lanthanide metals

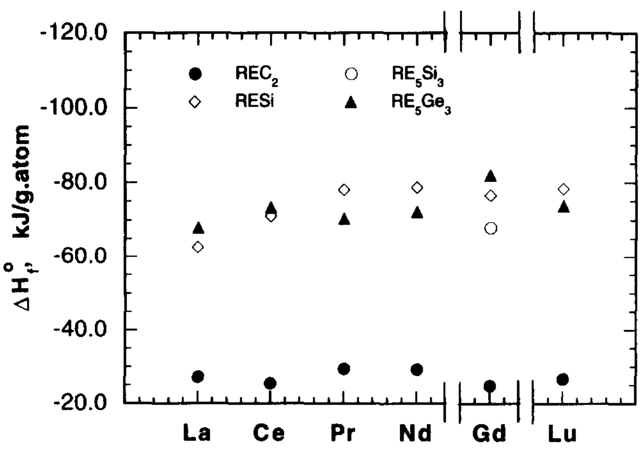

Fig. 1. Standard enthalpies of formation for characteristic carbides, silicides and germanides of La,Ce,Pr,Nd,Gd and Lu. The broken axes indicate that elements for which we do not report data are missing between Nd and Gd and between Gd and Lu.

previously studied in this laboratory. The value for La_5Ge_3 was reported by Jung and Kleppa [5]. The plotted value for LaSi was calculated from e.m.f. data by Samsonov et al. and cited by Schlesinger [35]; all the other values were reported by the present authors [6–8].

Note that in this figure we give the enthalpies of formation of REC_2 for the carbides, of RESi and RE_5Si_3 for the silicides ($LuSi_2$ does not form at our calorimeter temperature) and of RE_5Ge_3 for the germanides. The heats of formation of some other phases in these systems are included in Refs. [7,8]. Fig. 1 shows that the values in each set of compounds are quite comparable for all the lanthanide metals from La to Gd and Lu. The heats of formation for the Lu compounds are of special importance since Lu is the end member in the lanthanide series. It is therefore of special interest to ascertain any systematic increase or decrease in the enthalpies of formation from La to Lu. Fig. 1 shows that the values of the enthalpies of formation for compounds with the same stoichiometry and crystal structure are very nearly constant. Note that the heat of formation of LuB_2 is considerably less exothermic than the values for the tetraborides and hexaborides of the earlier lanthanide metals [9]. This difference clearly reflects the change in structure. It also correlates with the fact that LuB_2 has a significantly lower melting point than LuB_4 and the other lanthanide tetraborides.

In Table 3 we compare our value of ΔH_f^0 for Lu_5Sn_3 with the calorimetrically determined enthalpies of formation for some other RE_5Sn_3 phases. Among these phases La_5Sn_3 and Ce_5Sn_3 were studied by Borzone et al. [22–24] and Sm_5Sn_3 by Percheron et al. [25]. Clearly our value for the enthalpy of formation of Lu_5Sn_3 compares well with those for La_5Sn_3 and Ce_5Sn_3, but is somewhat more exothermic than the reported value for Sm_5Sn_3. This again suggests a relatively small change in the enthalpies of formation from La to Lu.

In Fig. 2 we compare our new enthalpies of formation for Lu carbides, silicides and germanides with values for compounds with other Group IVB elements such as Sn and Pb. The value for Lu_5Sn_3 was determined in the present study, while the value for $LuSn_3$ was calculated by Bayanov et al. [19] from e.m.f. data. The value for $LuPb_2$ was determined by Borzone et al. by calorimetry [36]. A very similar value for $LuPb_2$ may be estimated from the e.m.f. study of liquid Lu–Pb alloys by Roshchina and Bayanov [37].

Table 3
Comparison of enthalpies of formation (kJ g.atom^{-1}) for some RE_5Sn_3 phases measured by calorimetry; references in parentheses

Compound	ΔH_f^0	
La_5Sn_3	-77.4 ± 2.1 [22]	-73.2 ± 4.2 [23]
Ce_5Sn_3	-73.2 ± 4.2 [24]	-75.3 ± 4.2 [23]
Sm_5Sn_3	-63.6 ± 3.4 [25]	
Lu_5Sn_3 [a]	-73.6 ± 1.4	

[a] Present work.

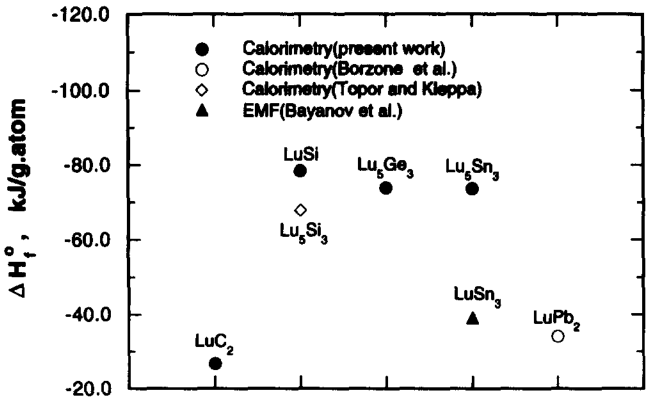

Fig. 2. Standard enthalpies of formation for characteristic compounds of Lu with group IVB elements C,Si,Ge,Sn and Pb.

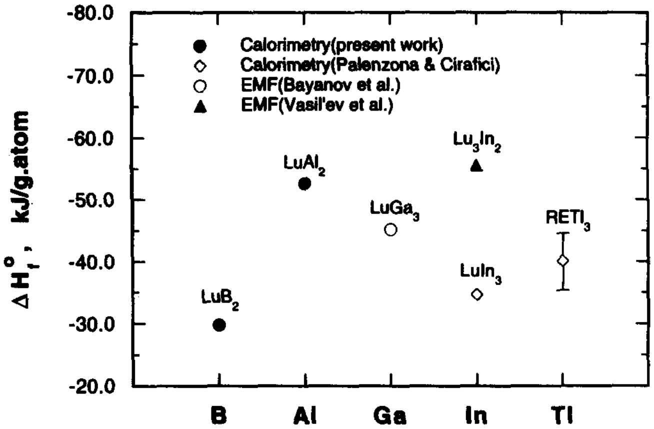

Fig. 3. Standard enthalpies of formation for characteristic compounds of Lu with group IIIB elements B,Al,Ga,In and Tl. The value for $RETl_3$ represents an average of values for $RETl_3$ compounds as published by Palenzona and Cirafici [27].

We noted in our earlier communications that the enthalpies of formation of early lanthanide elements with the IVB elements in the periodic table show a roughly parabolic correlation [7,8]. Fig. 2 shows that a similar correlation may exist also for the Lu compounds. However, we note that the increase in magnitude from C to Si is larger than in the early lanthanide systems, and that the subsequent changes from Si to Ge and Sn are smaller if we limit our comparison to the 5:3 stoichiometry. The difference between the plotted values for Lu_5Sn_3 and $LuSn_3$ is very large. It clearly cannot be accounted for by the difference in the Lu concentration of Lu_xX_{1-x}, the corresponding values of $x(1-x)$ for Lu_5Sn_3 and $LuSn_3$ being 0.2344 and 0.1875 respectively.

In Fig. 3 we compare our enthalpies of formation for LuB_2 and $LuAl_2$ with values for compounds of Lu with other group IIIB elements such as Ga, In and

Tl. The value for $LuGa_3$ was derived by Bayanov et al. from e.m.f. data [28]. The value for Lu_3In_2 was calculated by Vasil'ev et al. from e.m.f. measurements [26]. The enthalpy of formation for $LuIn_3$ was reported by Palenzona and Cirafici from calorimetry [27]. We found no experimental heat of formation for any alloy in the Lu–Tl system; the plotted point represents an average for $RETl_3$ compounds measured calorimetrically by Palenzona and Cirafici [27].

We note that similarly to Fig. 2 the change in the heat of formation from B to Al is relatively large compared to the changes from Al to Ga to In. The difference among the plotted values for the Lu–In system are substantial, and well beyond what one would expect from a simple $x(1-x)$ dependency. In view of the noted differences in molecular compositon, structure and measurement techniques, we cannot find a basis for any functional relationship in this graph.

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